Determination of the friction coefficient of a Brownian particle by molecular-dynamics simulation

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Abstract

By using the Kirkwood formula, the friction coefficient of a solvated Brownian particle is determined from the integration on time of the autocorrelation function of the force that the solvent exerts on this particle. Extensive molecular dynamics simulations show that above a definite size of the studied systems the value of the integral defining the friction coefficient goes to a quasi constant value (a plateau) when the upper bound on time increases. The minimal value of the system size where the integral exhibits this asymptotic behavior, rises with the Brownian particle size. From the plateau, a reliable estimate of the friction coefficient is obtained.

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In solutions, it is supposed that the large particles such as micelles or colloids which coexist with the atoms, ions or small molecules of the solvent behave as Brownian particles. At low concentrations of the large particles, by using multi-scale analysis [1–4], this hypothesis has been justified in the limit where the ratio between the mass of the solvated particles and that of the solvent molecules goes to ∞. It has then been established that the diffusion coefficient of Brownian particles can be computed in term of the friction coefficient characterizing the force exerted on them by the solvent. When the Brownian particles have

a quasi-macroscopic size, from hydrodynamic arguments the Stokes [5] law can be derived. It gives an expression of the friction coefficient $\xi = CR\eta$ where R is the size of the particles, η the viscosity of the solvent and C a numerical coefficient depending on the possible choices of boundary conditions at the interface between solvated particles and solvent.

However in many suspensions, such as ionic solutions, the values of ratios of masses and sizes between the solvated particles and solvent molecules are only of the order of 10 and the possibility that the solvated particles can be considered as Brownian particles becomes questionable. Several theoretical works [6,7] and works based on numerical simulations [8–11] have been devoted to this question. The main problem addressed in these works was that of the determination of the lower bounds of the size and mass ratios above which, to a good approximation, the motion of the solvated particles is Brownian. The criterion chosen to locate these bounds was that the diffusion coefficient of the solvated particles obeys to the relation between the diffusion coefficient D and friction coefficient ξ strictly valid only for brownian particles $D = k_B T/\xi$ (k_B is Boltzmann's constant, T the temperature of the solvent). The main concern, when the Stokes estimate of ξ is used, is the choice of the hydrodynamic boundary condition between solvated particles and solvent which is well defined only when the solvated particle has a macroscopic size. This last shortcoming can be overcome by computing ξ from its exact expression for a Brownian particle derived by Kirkwood [12] and later, more rigourously, from multi-scale analysis [2,13]. Obviously this method seems the correct way to proceed in order to check the brownian behavior of a solvated particle. However, as it was discussed in the literature [8,10,12,14–16], this method is not easy to use in simulations due to important finite size effects. This work is devoted to discuss this problem and to establish in what conditions, in a numerical simulation, the friction coefficient of a solvated particle of large mass and size can be credibly determined.

The friction coefficient ξ is given in terms of the integration on time t of the equilibrium autocorrelation function $< \mathbf{F}(0) \,.\, \mathbf{F}(t) >$ of the instantaneous microscopic force $\mathbf{F}(t)$ experienced by the Brownian particle :

$$\xi = \frac{1}{3k_BT}\int_0^\infty < \mathbf{F}(0)\,.\,\mathbf{F}(t) > \, dt\,. \tag{1}$$

This expression of the friction coefficient has the same form as the Green-Kubo relations used to calculate the transport coefficients.

For finite size systems, the computation of ξ from Eq. (1) and, more generally, that of the transport coefficients from Green-Kubo relations are confronted with a problem that we illustrate for this specific case. From the momentum conservation, the force $\mathbf{F}(t)$ acting on one Brownian particle in a solvent of N molecules is given by

$$\mathbf{F}(t) = -\frac{d\,\mathbf{P}(t)}{dt} \equiv -\dot{\mathbf{P}}(t) = -\sum_{i=1}^{N} m\frac{d\,\mathbf{v}_i(t)}{dt}\,, \tag{2}$$

where m is the mass of the solvent molecules with velocities $\mathbf{v}_i(t)$ $(i = 1, ..., N)$ and ξ_N can be written as

$$\begin{aligned}
\xi_N &= \lim_{t\to\infty} \xi_N(t) && (3)\\
&= \frac{1}{3k_BT}\lim_{t\to\infty}\int_0^t < \mathbf{F}(0)\,.\,\mathbf{F}(\tau) >_N \, d\tau \\
&= \frac{1}{3k_BT}\lim_{t\to\infty,\,s\to\infty}\int_0^t d\tau\frac{d}{d\tau}\frac{1}{s}\int_0^s \mathbf{F}(u).\mathbf{P}(\tau+u)\,du \\
&= -\lim_{t\to\infty}\frac{< \dot{\mathbf{P}}(t).\mathbf{P}(0) >_N}{3k_BT} + \frac{< \dot{\mathbf{P}}(0).\mathbf{P}(0) >_N}{3k_BT}. && (4)
\end{aligned}$$

The last term of Eq. (4) vanishes by symmetry on time and it is expected that, for $t \to \infty$, the first term also vanishes due to the loss of correlations between $\dot{\mathbf{P}}(\infty)$ and $\mathbf{P}(0)$, according to the ergodic postulate of the equilibrium statistical mechanics, with the final result that ξ_N should be zero. The well known way to overcome this paradox is that the thermodynamic limit on N must be taken before that the limit $t \to \infty$ is performed. The argument can be summarized by guessing that at large values of t and N, $\xi_N(t)$ can be written in the form $c\,g(at/N)$ where c and a are coefficients independent of N and $g(at/N)$ is a decreasing function of t equal to 0 at $t = \infty$ and normalized to 1 at $t = 0$. By perfoming the thermodynamic limit $N \to \infty$ before the limit $t \to \infty$, ξ is given by $\lim_{t\to\infty}\{\lim_{N\to\infty}\xi_N(t)\} = c$ and ξ is now finite.

If in simulations N is large enough, it can be expected, following the remark made by Kirkwood in [12], that, in the range of values of t where $\xi_N(t)$ reaches its asymptotic form $\simeq c\, g(at/N)$, t is such as $t << a/N$. In this domain of t, $\xi_N(t)$ is given by $\xi_N(t) \simeq c + acg'(0)t/N$ and presents a quasi plateau or a slow linear decay with t from which the value of ξ in the thermodynamic limit can be estimated.

As it was proposed, for instance, in [6,10] it is possible to give a specific analytic form to $g(at/N)$ by supposing that, following the Onsager's principle, the regression of the fluctuations of $\mathbf{F}(t)$ at large t is governed by the laws of the macroscopic hydrodynamics. According to these laws, the force exerted by the solvent on the Brownian particle is proportional to the momentum $\mathbf{P}(t)$ carried by the solvent, i.e.

$$\mathbf{F}(t) = \frac{\xi_o}{Nm}\mathbf{P}(t) \tag{5}$$

a relation which implies that

$$< \mathbf{P}(t)\,.\,\mathbf{P}(0) >_N = 3Nmk_BT \exp(-\frac{\xi_o}{Nm}t) \tag{6}$$

and then

$$\xi_N(t) = -\frac{< \dot{\mathbf{P}}(t)\,.\,\mathbf{P}(0) >_N}{3k_BT} = \xi_o \exp(-\frac{\xi_o}{Nm}t). \tag{7}$$

At large N and t such as $t << \xi_o/Nm$, an expansion of the exponential yields to a linear expression, similar to that of $\xi_N(t)$ given above, allowing to determine the friction coefficient as

$$\xi_N(t) = \xi_o\,(1 - \frac{\xi_o}{Nm}t + \,...\,)\,. \tag{8}$$

In order to investigate the possibility of a computation of ξ following the procedure describes above, we have realized a set of molecular-dynamics simulations with increasing values of N.

The studied systems are made of N molecules of solvent enclosed in a periodic cubic box of volume V. In this box, a particle is immersed and supposed to have a size and mass M

large compared of those of the solvent molecules. Hence the mass of this particle satisfies to the condition required so that the relation between D and ξ, given above, applies. When M is large, it is possible to consider that, in the time scale accessible in a simulation, the particle is immobile.

The molecules and the fixed particle interact through a Lennard-Jones (LJ) potential modified with a cubic spline, as describe in a previous paper [11]. This potential has the form $v_{ij}(r) = \epsilon_{ij} f(r/\sigma_{ij})$ where the indices $i, j = 1$ or 2 refer to the solvent and fixed particle, respectively. The parameters σ_{ij} are such as $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$, and ϵ_{ij} are equal $\epsilon_{12} = \epsilon_{22} = \epsilon_{11}$. The unit of time is chosen equal to $\tau_0 = \sqrt{(m\sigma_{11}^2/\epsilon_{11})}$ and that of energy, length, and mass are chosen, respectively, equal to ϵ_{11}, σ_{11}, and m. The values of the solvent density and temperature are $\rho^* \equiv N\sigma_{11}^3/V \simeq 0.84$ and $T^* \equiv k_B T/\epsilon_{11} = 1.0$, thus specifying a dense liquid state near the triple point of the LJ system. The simulations were realized at constant energy using the standard Verlet algorithm [17], with a time step $\Delta t = 0.005\,\tau_0$. Typical simulation runs are carried out for 20000 equilibration time steps followed by 4 to 8 millions time steps. During the runs, the time autocorrelation function of $\mathbf{F}(t)$ is computed over a sequence of blocks of $4000\Delta t$ to allow an evaluation of statistical errors. We have considered two different sizes for the Brownian particle, namely $\sigma_{22} = 4.0$ and 7.0 and systems of increasing values of N : 864, 1500, 5324, 12000, 32000 and 55296. In order to maintain constant the value of the pressure, the volume of the simulation box was slightly increased, when σ_{22} was varied from 4.0 to 7.0.

We first discuss the case of $\sigma_{22} = 4.0$. In Fig. 1, we show $\xi_N(t)$ as a function of reduced time t/τ_0. When N is increased from 864 to 32000, the behavior of $\xi_N(t)$ changes drastically in the domain of $t/\tau_0 > 5.0$. For the low values of N, $\xi_N(t)$ goes rapidly to zero and for the two larger values of N, it is almost constant. Qualitatively, this behavior of $\xi_N(t)$ at large time corresponds to that expected when N increases. In particular, if this behavior is described by Eq. (7), the results presented in Fig. 1 can be interpreted as the transition between the exponential decrease of $\xi_N(t)$ given by Eq. (7) and the linear decrease, at large N, given by Eq. (8). Quantitatively, it should be possible to obtain the value of ξ from the

fit of $\xi_N(t)$, for t/τ_0 between 12 and 20, to an exponential form when N is $\simeq 1000$ and a linear form when N is $\simeq 20000$.

However, the possibility that the values of ξ, determined from the fits made at different values of N, coincide within the statistical uncertainties, supposes that finite size effects, in particular those associated to the use of the periodic boundary conditions, do not affect the long time behavior of $\xi_N(t)$. From the fit of the multiplicative constant of the exponential (cf. Eq. (7)) the estimates of ξ are : 219.4 ($N = 864$), 144.7 ($N = 1500$) and 122.9 ($N = 5324$) and from that of the constant term in the linear form (cf. Eq. 8) they are : 113.3 ($N = 12000$) and 110.7 ($N = 32000$). Clearly, for the two large systems these values of ξ agree within the statistical error equal to 10-15%. But the factor of 2 between the values found at $N = 864$ and $N = 32000$ must be attributed to finite size effects. The side lenghts L of the simulation cells being for these two values of N equal to ~ 10 and ~ 35, due to the periodic boundary conditions the fixed particle is distant from these nearest replica by the same lengths. The sound velocity c_s of the solvent, for the considered thermodynamic state, being in reduced units ~ 6, gives typical times L/c_s of 1.5 and 6 beyond of which the finite size effects resulting from the mutual influence between the fixed particle and its replicas can affect the correlation function. The magnitude of these effects on the value of ξ is difficult to assess. It has been quantitatively discussed only for the bulk values of the transport coefficients of diffusion or viscosity in dense fluids [18], corrections of about $\sim 10\%$ have been found for systems of $N \sim 1000$ molecules and they seem much larger on ξ. Other estimates of ξ are obtained from the fit of the coefficient of t in the exponential (Eq. (7)) or the linear approximation (Eq. (8)). For the small values N, we obtained 205.5 ($N = 864$) and 143.3 ($N = 1500$), for the large values of N, 98.4 and 91.1. These results seem to confirm that the asymptotic behavior of $\xi_N(t)$ is well described by Eq. (7) taking into account the finite size effects.

FIGURES

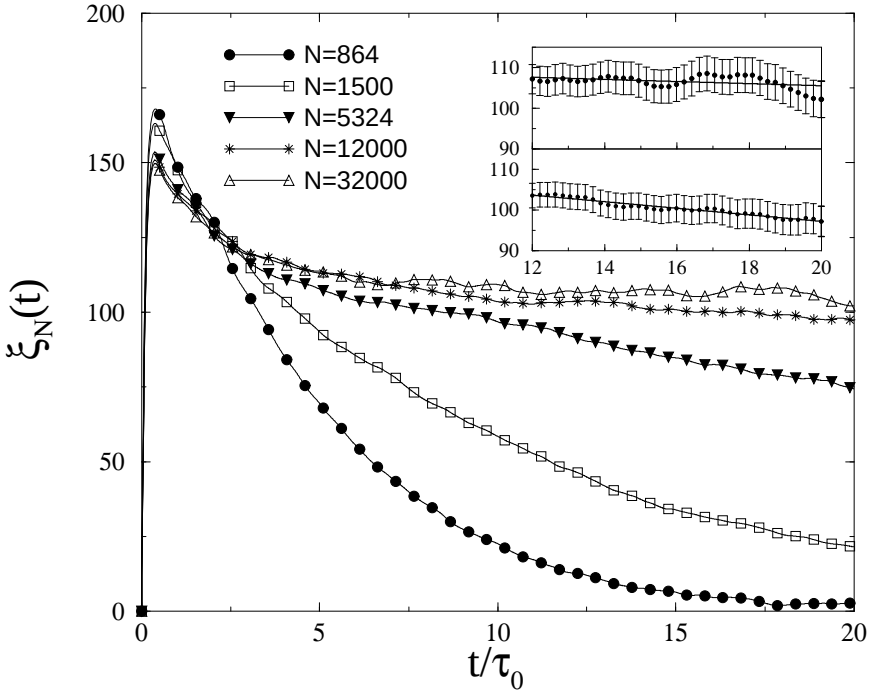

FIG. 1. $\xi_N(t)$ for the fixed particle of size $\sigma_{22} = 4.0$ and increasing values of N. Insert : asymptotic behavior with error bars and its linear fit at $N = 12000$ and 32000

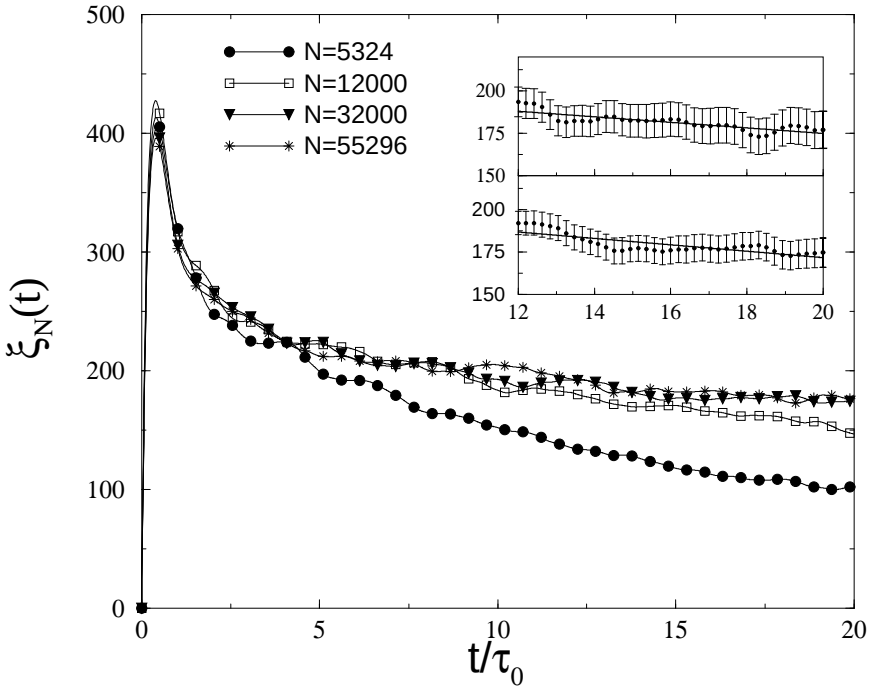

FIG. 2. $\xi_N(t)$ for the fixed particle of size $\sigma_{22} = 7.0$ and increasing values of N. Insert : asymptotic behavior wih error bars and its linear fit for $N = 32000$ and 55296

We consider now the case of the fixed particle with a size $\sigma_{22} = 7.0$. The $\xi_N(t)$ functions are plotted in Fig. 2. for N equal to 5324, 12000, 32000 and 55296. The behavior of $\xi_N(t)$, when N increases, is similar to that obtained with the particle of size $\sigma_{22} = 4.0$, but it is only for $N \geq 32000$ that $\xi_N(t)$ presents a slow linear decrease for $t/\tau_0 > 10.0$. For the particle of size $\sigma_{22} = 4.0$, we remark that this latter behavior is reached for systems smaller by a factor ~ 2 and, then, the size of the fixed particle has an important influence on the value of the system size where $\xi_N(t)$ exhibits a slow linear decrease at large time. This remark is confirmed by the results of the fits of $\xi_N(t)$ by an exponential at $N = 5324$ and 12000 or a linear function at $N = 32000$ and 55296. The values of ξ are 217.0, 244.2, 209.3 and 207.5 respectively. We notice that, the linear behavior of $\xi_N(t)$, at large t, corresponds obvioulsy to the fact that $< \mathbf{F}(0) \,.\, \mathbf{F}(t) >$ decreases very slowly in the same domain of t. This point is illustrated in Fig. 3 where this behavior is clearly seen for $N = 12000$, 32000 and 55296 within statistical errors.

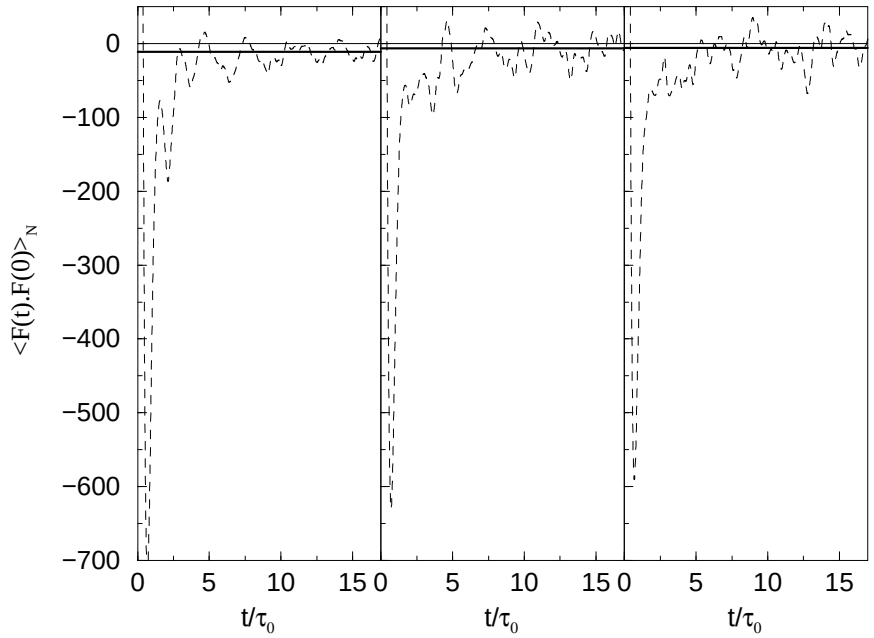

FIG. 3. Autocorrelation function $< \mathbf{F}(0) \,.\, \mathbf{F}(t) >_N$ for the particle of size $\sigma_{22} = 7.0$ at $N = 12000$, 32000 and 56296. Solid lines : estimate of its almost constant value from its average for $t/\tau_0 > 12.0$ and < 20.0 : $\sim$ -12.6, -6.6 and -6.1.

From the results of the present simulations it seems needed to adopt a critical point of

view on the previous works made in order to determine the friction coefficient of a brownian particle and to check when a particle of large masses and sizes can be considered as a brownian particle. The most important criticism is that, in these works the sizes of the system studied in the simulations were too small. This remark applies, for instance, to the simulations presented in [6] where the friction coefficient of a fixed hard sphere of diameter $4d$ in a solvent made of hard spheres of diameter d was computed at a density $\rho d^3 \simeq 0.471$. Such a computation corresponds closely to that made in this work for a fixed particle with $\sigma_{22} = 4.0$. In [6], the largest considered system had a size of $N = 1500$ which, as discussed above, seems too small to obtain a good estimate of ξ from an exponential fit of $\xi_N(t)$ at large times and, then, to check the validity of Stokes estimate of ξ. The system size used in [10] for the computation of the friction coefficient of a fixed particle in a LJ type system being of the order of $N = 1000$, finite size effects should also affect the simulation data.

As mentionned already, the asymptotic form of $\xi_N(t)$ at large times has been discussed in many works in the literature, for instance in [14], [15] and [16], in particular the question of the occurence of a domain of time where the friction coefficient $\xi_N(t)$ should exhibit a plateau. It has been proposed in [8] to bypass the search of such a plateau in $\xi_N(t)$ by computing ξ from the integration of $< \mathbf{F}(0) \,.\, \mathbf{F}(t) >$ from $t = 0$ to the value of $t = t_1$ where, for the first times when t increases, $< \mathbf{F}(0) \,.\, \mathbf{F}(t_1) >$ becomes 0. In our simulations $t_1/\tau_0 \simeq 0.5$, clearly from the comparison between Fig. 2 and Fig. 3 of $\xi_N(t)$ and $< \mathbf{F}(0) \,.\, \mathbf{F}(t) >_N$, such a method to estimate ξ seems problematic since the value of $\xi_N(t_1)$ for instance at $N = 55296$ does not agree with the value ξ obtained from the analysis of the asymptotic behavior of $\xi_N(t)$.

Since the present simulations show that system sizes of $N \simeq 20000$ are needed to correctly estimated ξ, it is expected that similar system sizes are needed to compute D in order to avoid finite size effects. For instance in [11] for $N = 5324$, for a brownian particle with $\sigma_{22} = 4.0$ and $M = 60$ in a LJ solvent at a thermodynamic state identical to that considered here, it was found $D = 0.077$. By using $D = k_B T/\xi$ this value of D agrees well with that of $\xi \simeq 120$ obtained in this work at $N = 5324$, but it differs by 10% from that, computed at

$N = 32000$, $\xi \simeq 110$. A new determination of D at $N = 32000$ gives $D = 0.095$, which now agrees with our estimate of ξ at the same value of N from the slow linear decay of $\xi_N(t)$ for $t/\tau_0 > 12$.

In conclusion from our simulations realized for increasing system sizes from $N \sim 1000$ to ~ 56000, we have shown that the qualitative behavior of $< \mathbf{F}(0) \,.\, \mathbf{F}(t) >$ and, consequently, that of $\xi_N(t)$ is in excellent agreement with that guessed by Kirwood [12] and in subsequent works. [15,16]. For large times, the representation of $\xi_N(t)$ by Eq. (7), derived from a simple argument based on Onsager principle, seems an adequate model of this asymptotic behavior. From a quantitative point of view, in spite of simulation runs totalizing 4 to 8 millions of time steps the statistical uncertainties on the friction coefficient stay of the odrer of 15%, a reduction of this uncertainty by a order of magnitude seems beyond what it is possible to make by using present standard computers. We stress that the aim of this work was the investigation of the variation of $\xi_N(t)$ with N. In the thermodynamic limit, the asymptotic behavior of $\xi_N(t)$ should be an algebraic decay at very large time. It was not considered here, in particular, because its amplitude is much smaller than the present uncertainties on $\xi_N(t)$ in this domain of time [11,18].

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